# Study of Crystallite Size of Yttria-Stabilized Zirconia powders by Rietveld Method

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**Abstract.** The yttria-stabilized zirconia (YSZ) is used in a great variety of applications, for example, electrolytes of solid oxide fuel cells and oxygen sensors. In the study of YSZ, the particle size powders and sintering processes are important to define the final properties of the zirconia products. The objectives of this work were to determine the phases and the crystalline size using X-Ray Diffraction (XRD) data and the Rietveld Method (RM) of the YSZ powders obtained by chemical synthesis based on the Pechini method. It was used $ZrOCl_2.8H_2O$ and $Y(NO_3)_3.5H_2O$ as precursors reagents. After calcination at 550$^oC$ during 24 hours, the powder was analyzed by XRD and scanning electronic microscopy (SEM). From XRD and using Rietveld method were verified that there is only cubic phase with lattice parameter a = 5.1307(1) Å and the space group Fm3m. Due to substitution of the Zr atoms in the Y atoms sites, there were vacancies in 17.72 % of O atoms sites. However, the percentage of substitution of Zr atoms in Y atoms sites in the structure not was determinate because the curves of atomic scattering of them are very similar. Using Scherrer equation and considering anisotropy effect, the average crystalline size was determinate: 10,43 nm (c axis) and 10,39 (b axis). This spherical symmetry also observed for SEM.

## Introduction

Zirconia is a widely used material because of its unique properties. In fact, its mechanical properties, specially hardness and strength, combined with good oxygen ionic conductivity make this material appropriate for many applications such as coatings, catalyst support, oxygen sensors and solid electrolyte in solid oxide fuel cells (SOFCS) [1,4].

It is known that up to 1170 °C the zirconia is stable in the monoclinic phase, from 1170 to 2370 °C in the tetragonal phase and above 2370 °C in the cubic phase. However, it is possible to obtain the cubic and tetragonal phases in room temperature, using small quantities of dopants oxides [5,6]. Addition of small quantities of oxides such as CaO, MgO or $Y_2O_3$ to zirconia stabilizes certain phases at room temperature. Amongst several of stabilized zirconia, $Y_2O_3$ stabilized $ZrO_2$ (YSZ) has become one of the most important and widely used for various applications such as oxygen sensors, fuels cells and catalytic membrane because of its good oxygen ionic conductivity and good mechanical properties at elevated temperature [7,8]. By appropriate adjust $Y_2O_3$ concentration in the lattice $ZrO_2$, it is possible to retain different phases of $ZrO_2$ [7]. Stabilization of cubic phase can occur due to substitution of $Y^{+3}$ for $Zr^{+4}$ in

the cubic structure; the substitution of the Zr atoms generates oxygen vacancies in the cubic structure [6].

Several chemical and physics methods have been adopted to synthesize cubic $ZrO_2$, such as thermal decomposition, hydrothermal route, sol-gel method, chemical evaporation [6,9-12]. These methods generally produce powders with different morphology, chemical composition, and crystallite size. These powders characteristics are important because they determine final microstructure of zirconia ceramics and consequently its properties.

The objectives of this work were to determine the phases and the crystalline size using X-Ray Diffraction (XRD) data and the Rietveld Method (RM) of the YSZ powders obtained by chemical synthesis based on the Pechini method.

To analyze the zirconia applications it is important to know the physical characteristics of the crystalline structure of this, which the percentile of generated vacancy of oxygen due to substitution of Zr for Y, the percentile of atoms of Zr that are substituted by the of Y and the crystallite size are formed in the calcination process.

The Rietveld method (RM) is widely used in polycrystalline crystallography and materials science. It is a least-square whole-pattern-fitting structure refinement method, performed until the best fit is obtained between the complete observed powder diffraction pattern and entire calculated pattern. This whole calculated pattern is based on the simultaneously refined models for composition and crystal structure of each phase, diffraction optic effects, instrumental factors and other specimen characteristics that can be modeled. [13,14,15].

In the RM a reflection profile function approximates the instrumental and samples features [15]. The profile function chosen in this work is the function Modified Thompson-Cox-Hastings pseudo-Voigt [16], given by the equation (1).

$$\Phi PVTCH = \eta L + (1-\eta)G \qquad (1)$$

where L and G are Lorentz and Gauss functions, respectively, $\eta$ is the mixing parameter that takes into consideration the components of the Gauss and Lorentz full-width-at-half-maxima (FWHM) of the diffraction peak profile. P. W Stephens [17] proposed a phenomenological model for the anisotropic broadened of the profile, considering a distribution of the metric parameters of the lattice. The determination of the crystallite size is carried out by the equations 2 and 3.

$$p \parallel = \frac{18000k\lambda}{\pi(X + X_e)} \qquad (2)$$

$$p \perp = \frac{18000k\lambda}{\pi X} \qquad (3)$$

where k is the Scherrer constant, X and $X_e$ are the coefficients of anisotropic broadened due to distribution of the crystallite sizes [18].

## Experimental procedure

The powders of yttrium-doped zirconia, with compositon $ZrO_2$ + 4.5%mol $Y_2O_3$, were prepared using a chemical synthesis based on the Pechini method. In this method the zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) and yttrium nitrate hexahydrate

($Y(NO_3)_3.6H_2O$) were dissolved in formic acid (REAGEN), then polyethylene glycol was added (MW ≈ 1500 g / mol) (CRQ). After complete dissolution of the polymer, the mixture remained under agitation for about 30 minutes. The resin was kept at 105 °C for 24 hours to remove water produced during the synthesis. The calcinations of the resin were carried out at 550°C for 24h.

After being calcined, powders were crushed in an agate mortar and were characterized by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) for the analysis of phase formation and measurement of crystallite size.

In order to use the RM, XRD data were collected using a Shimadzu - XRD-6000 diffractometer operating at 40 kV and 30 mA with Cu$K\alpha$ radiation, in the step-scan mode over a range 22° - 70° 2θ, step size of 0.02° 2θ and a counting time of 2 s/step. The refinement Rietveld was applied using the program GSAS.

The morphology of $ZrO_2$ powders was examined using Shimadzu - SSX-550 scanning electron microscope (SEM).

## Results and Discussion

Figure 1 shows the result of the XRD pattern adjustments by RM (Rietveld refinement plot). It is possible to verify the behavior of the angular variation of FWHM of the diffraction peak, indicating the anisotropic behavior of FWHM in the profile, as presented in figure 2.

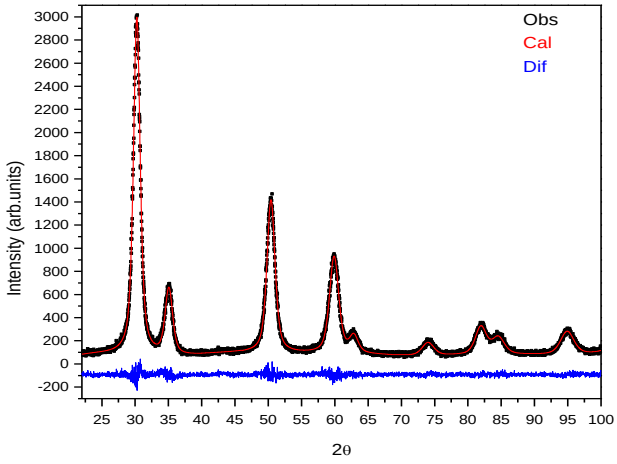


**Figure 1**: Rietveld refinement plot for the powder calcined at 550°C: in red is the calculated diffraction pattern, in black is the observed diffraction pattern and in blue is the difference among observed and calculated diffraction pattern.

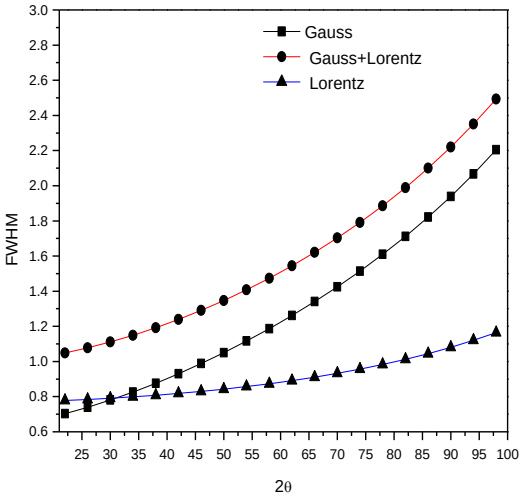


**Figure 2**: Behavior FWHM in function of 2θ.

It is observed in figure 2 that FHWM for the Gauss function increases more quickly than the one of Lorentz, and the combination of the two results in an ascending curve in function of 2θ. This behavior indicate anisotropic effects present in the sample, belonging one to them a distribution of the crystallite sizes, as the model proposed by P. W Stephens [17].

The crystal structure proposal for the yttria-cubic stabilized zirconia is the same of fluorite [19]. They are isostructural and belong to the space group Fm3m. The atomic positions are special positions of the space group Fm3m and they are not adjusted in the refinement. It is known that in yttria stabilized zirconia, there is a substitution of the Zr atoms for the Y atoms [6], however in the Rietveld refinement is not presented a convergence that can be considered physically coherent because the Zr and Y atomic scattering factors are close, these are shown in the Figure 3 for the Cukα radiation, and disabling to identify the substitution degree of these atoms in the stabilized structure.

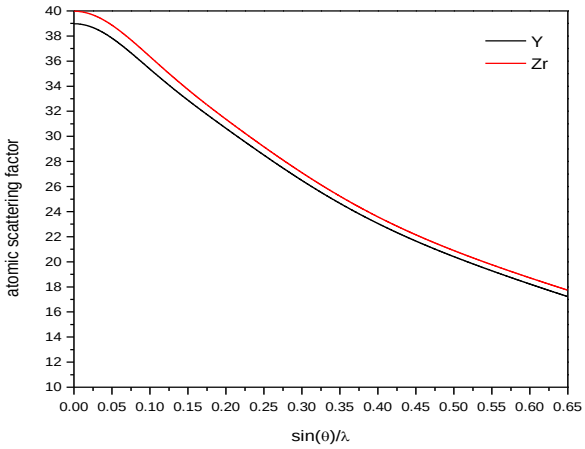


**Figura 3:** Atomic scattering factor for atoms Zr and Y, Cukα Radiation.

The refinement indicated that due to substitution of Zr for Y, occurs the creation of oxygen vacancies. The generated vacancy percentile was of 17.72%. It is well known that

these generated vacancies are important, because they give the necessary characteristics for the application of sensor devices of oxygen [6].

The Rietveld refinement was finished when shows best fit by the least-squares method and disagreement indexes were stabilized. These indexes evaluate the adjustment accomplished by RM and also how close the structure proposal is in agreement with the real structure for sample. This indexes converged for Rwp (7.17%), Rp (5.18%), $\chi 2$ (1.25) and Dwd (1.77), 1.932 <Dwd <2.068, and the factor that evaluates the quality of the proposed structure, RF2 (1.81%).

The parameter found were – lattice parameter, a = 5.1307(1) Å; the cell volume 153,03(1) $Å^3$; the density 5.80(9) $g/cm^3$.

As for the crystallite size, considering the anisotropic effects found in the diffraction profile, the average crystallite size determinate was: 10.43 nm (c axis) and 10.39 (b axis). It can be observed that the crystallites are practically spherical.

Figure 4 presents a micrograph obtained by SEM of the powder. It is not possible observed the individual crystallite, only particle agglomerates with spherical symmetry.

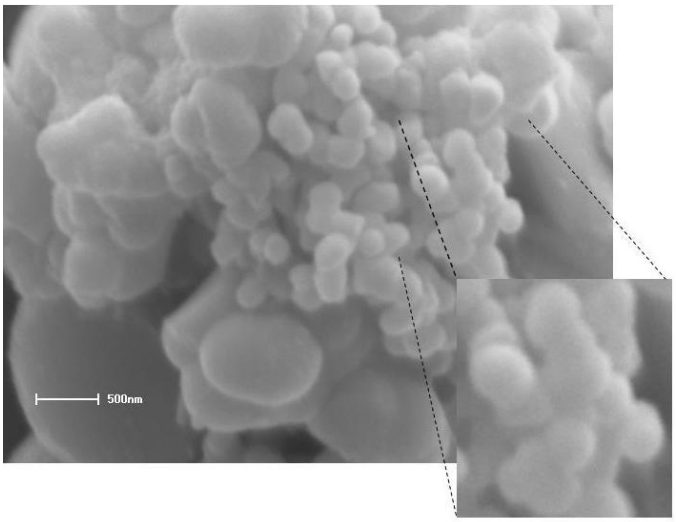


**Figura 4:** SEM image of the sample calcined at 550$^oC$.

## Conclusion

From XRD and using Rietveld method were verified that there is only cubic phase with lattice parameter a = 5.1307(1) Å and the space group Fm3m. This structure proposal for the yttria stabilized zirconia presented low percentile mistake. However the XRD not to make possible to indicate the degree of substitution of Zr and Y atoms, because the curves of atomic scattering of them are very similar, but it indicated that substitution exists due to formation of oxygen vacancies. Due to substitution of the Zr atoms in the Y atoms sites, there are 17.72 % of oxygen vacancies. As the diffraction profile presented anisotropic behavior of FWHM, the model of P. W Stephens can be used. Using Scherrer equation and considering anisotropy effect, the average crystalline size was determinate: 10.43 nm (c axis) and 10.39 (b axis). This spherical symmetry also observed for SEM in the agglomerate powders.

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